Supporting Information

On the nature of organic catalysis "on water"

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S1. Bimolecular rate constants for the dilute and neat reactions (Appendix).

S2. Full citation for ref. 83.

S3. Structures and energies of the stationary points along the neat reaction pathway.

S4. Structures and energies of the stationary points along the surface reaction pathway.

S1. **Bimolecular rate constants for the dilute and neat reactions (Appendix).**

For a bimolecular reaction in a dilute solution, a standard second-order rate equation is used to define rate constant, k_{bi}:

$$-\frac{d[A]}{dt} = k_{bi}[A][B] \tag{A1}$$

Introducing the progress variable, $x = a - [A] = b - [B]$, where a and b are initial concentrations of the species A and B, respectively, eq (A1) can be rewritten, after separation of variables, as

$$\int \frac{1}{(a-x)(b-x)}\,dx = -k_{bi}t\,. \tag{A2}$$

Integrating eq (A2) yields a well-known result for the standard second-order rate constant

$$k_{bi} = \frac{1}{t(a-b)}\ln\left(\frac{b[A]}{a[B]}\right). \tag{A3}$$

For the neat reaction, we define the rate constant in a slightly different way that takes into account the close proximity of the reactants. We introduce a mole fraction instead of a product of concentrations of both species since the probability of two reactants being near each other is already very high. In this way, the rate constants for the neat, aqueous homogeneous, and surface reactions, can be defined so as to have the same unit. Thus we write the rate equation for the neat reaction as

$$-\frac{d[A]}{dt} = k_N[A]Z_N n_B\,, \tag{A4}$$

where $a - [A] = b - [B]$ as above. The mole fraction of B at time t, n_B, when the products are in the same phase as the reactants, is then given as

$$n_B = \frac{[B]}{[A]+[B]+(b-[B])} = \frac{[A]-a+b}{[A]+b}. \quad \text{(A5)}$$

In this equation, we assume that via the b - [B] term, all the products remain in the organic phase. Substituting eq (A5) into eq (A4), after separation of variables, yields

$$\int d[A] \frac{[A]+b}{[A]([A]-a+b)} = -k_N Z_N t. \quad \text{(A6)}$$

Integrating eq (A6) gives

$$k_N = \frac{1}{Z_N t(a-b)} \left(b \ln \frac{[A]}{a} - a \ln \frac{[A]-a+b}{b} \right). \quad \text{(A7)}$$

The eq (A7) can then be simplified further for special cases, as considered in the Theory section of the text.

S2. Full citation for ref. 83.

Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'neill, D. P.; Distasio, R. A.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C. P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L.; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F.; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M., *Phys Chem Chem Phys* **2006,** *8*, 3172-3191.

S3. Neat Reaction (0 water molecule)

Barrier = 21.9 kcal/mol at UB3LYP/6-31+G*

Barreir after ZPE correction = 22.2 kcal/mol

Quadricyclane

B3LYP/6-31+G* (E = -271.4529224834), <S2> = 0.00

1	C	1.153424	-0.551580	0.000026
2	C	0.775587	0.710574	0.758767
3	C	-0.775530	0.710574	0.758799
4	C	-1.153470	-0.551500	-0.000025
5	C	-0.775534	0.710628	-0.758763
6	C	0.775584	0.710518	-0.758804
7	H	1.427472	1.233037	-1.450688
8	H	-1.427383	1.233267	-1.450593
9	C	-0.000055	-1.541502	0.000000
10	H	-0.000092	-2.181038	0.892532
11	H	-0.000064	-2.181038	-0.892531
12	H	-2.189924	-0.878324	-0.000046
13	H	-1.427379	1.233158	1.450671
14	H	1.427477	1.233148	1.450607
15	H	2.189854	-0.878484	0.000047

DMAD-trans configuration

B3LYP/6-31+G* (E = -566.4037154352), <S2> = 0.00

1	O	2.118670	-1.571531	-0.057936
2	O	2.438957	0.676442	0.128982
3	O	-2.118796	1.571556	0.057714
4	O	-2.438886	-0.676465	-0.128846
5	C	3.860486	0.521863	-0.098785
6	C	1.725857	-0.445016	0.118574
7	N	0.351956	-0.166264	0.483030
8	N	-0.351934	0.166366	-0.482914
9	C	-3.860459	-0.521949	0.098682
10	C	-1.725845	0.445030	-0.118415
11	H	4.292073	-0.125173	0.668470
12	H	4.267234	1.530179	-0.033996
13	H	4.034182	0.092987	-1.088206
14	H	-4.034337	-0.092999	1.088040
15	H	-4.291961	0.125000	-0.668695
16	H	-4.267142	-1.530292	0.033912

TS1

UB3LYP/6-31+G* (E = -837.8217412056), <S2> = 0.18

1	O	-1.398581	1.833787	-1.455215
2	O	-1.794961	2.333322	0.722429
3	O	2.752385	-0.689669	-0.615074
4	O	2.666546	1.382406	0.294725
5	C	-2.971828	3.044592	0.314859
6	C	-1.078398	1.776665	-0.280980
7	N	0.089654	1.212938	0.291164
8	N	0.742880	0.490398	-0.561239
9	C	-0.381961	-3.209285	-0.351019
10	C	0.400302	-2.261744	0.455559
11	C	-0.504269	-1.767357	1.592432
12	C	-1.814554	-2.758364	-0.261263
13	C	-1.811755	-1.689693	0.812508
14	C	4.093736	1.336239	0.465796
15	C	-0.005487	-1.457106	-0.784065
16	C	2.116913	0.293156	-0.270723
17	C	-1.517995	-1.298892	-0.622070
18	H	-2.707946	3.871918	-0.350441
19	H	-3.416411	3.420736	1.237221
20	H	-3.666884	2.377795	-0.204536
21	H	-2.128989	-0.649977	-1.234319
22	H	-0.540929	-2.493740	2.412803
23	H	0.019650	-3.945466	-1.035792
24	H	1.464763	-2.421665	0.597317
25	H	-0.196872	-0.791714	1.980454
26	H	4.372329	0.518082	1.135709
27	H	-2.676019	-3.329516	-0.585793
28	H	4.589909	1.199338	-0.498956
29	H	-2.744736	-1.378050	1.269708
30	H	0.495221	-1.528677	-1.737185
31	H	4.357838	2.299548	0.903220

M1 (intermediate)
B3LYP/6-31+G* (E = -837.8757530992), <S2> = 0.92

1	O	-0.966760	1.901563	-1.428199
2	O	-1.455760	2.468000	0.719325
3	O	2.712707	-1.194732	-0.465019
4	O	2.845348	0.963362	0.223173
5	C	-2.468169	3.361019	0.227949
6	C	-0.752101	1.809700	-0.227677
7	N	0.313506	1.159858	0.375012
8	N	0.791926	0.059606	-0.208890
9	C	-0.988629	-3.206412	-0.092975
10	C	-0.134748	-2.196710	0.613119
11	C	-1.165917	-1.482549	1.530124
12	C	-2.101804	-2.360750	-0.551806

13	C	-2.218265	-1.215281	0.454353
14	C	4.279370	0.836281	0.277801
15	C	0.011081	-1.141271	-0.580844
16	C	2.194464	-0.136326	-0.158151
17	C	-1.480906	-0.957974	-0.834851
18	H	-2.019262	4.146077	-0.387336
19	H	-2.928398	3.789783	1.118949
20	H	-3.209487	2.818320	-0.365331
21	H	-1.866431	-0.328622	-1.625202
22	H	-1.525922	-2.150117	2.320760
23	H	-0.631482	-4.105234	-0.584693
24	H	0.804627	-2.526156	1.053584
25	H	-0.785196	-0.561191	1.983663
26	H	4.565479	0.057047	0.988892
27	H	-2.942746	-2.706627	-1.141677
28	H	4.675994	0.593044	-0.711233
29	H	-3.172543	-0.743602	0.664636
30	H	0.532361	-1.594982	-1.423125
31	H	4.634453	1.812096	0.608768

TS2
B3LYP/6-31+G* (E = -837.8682880080), <S2> = 0.26

1	O	-1.517859	1.395268	1.354953
2	O	-2.116139	2.220889	-0.679032
3	O	0.040599	-2.778672	0.721434
4	O	-1.852027	-2.127495	-0.369615
5	C	-2.827154	3.257177	0.004337
6	C	-1.499654	1.307420	0.125511
7	N	-0.928916	0.337450	-0.665487
8	N	-0.248458	-0.601077	0.092627
9	C	3.327812	-0.085778	0.664451
10	C	2.332706	-0.856879	-0.112968
11	C	2.279946	-0.107655	-1.464983
12	C	3.071921	1.268596	0.367951
13	C	2.206446	1.307435	-0.884898
14	C	-2.323086	-3.483664	-0.311783
15	C	1.026377	-0.233477	0.643966
16	C	-0.646942	-1.917129	0.181674
17	C	1.337358	1.227977	0.306358
18	H	-3.589334	2.836369	0.666721
19	H	-3.293086	3.854392	-0.781836
20	H	-2.146474	3.876653	0.598419
21	H	0.846142	2.074389	0.766098
22	H	3.181994	-0.270004	-2.065051
23	H	3.884759	-0.449888	1.522351
24	H	2.373226	-1.942551	-0.102835

25	H	1.391885	-0.351912	-2.054670
26	H	-1.636375	-4.153476	-0.837036
27	H	3.522272	2.135116	0.834940
28	H	-2.424222	-3.809365	0.727088
29	H	2.201197	2.197847	-1.505279
30	H	1.073795	-0.470414	1.707135
31	H	-3.295125	-3.465821	-0.805646

Product
B3LYP/6-31+G* (E = -837.9523245286), <S2> = 0.00

1	N	0.052339	0.650104	0.743770
2	N	0.591260	-0.427574	-0.049352
3	C	0.090692	1.975130	0.347591
4	O	-0.676424	2.809742	0.800899
5	O	1.079792	2.217095	-0.527623
6	C	1.901546	-0.817670	0.201736
7	O	2.772610	-0.119460	0.674588
8	O	2.070514	-2.093776	-0.229741
9	C	1.276822	3.600892	-0.867692
10	H	2.118350	3.604937	-1.560882
11	H	1.513295	4.181511	0.027827
12	H	0.381146	4.010582	-1.342337
13	C	3.416348	-2.594316	-0.138304
14	H	3.364369	-3.622132	-0.499162
15	H	3.767241	-2.564788	0.896482
16	H	4.085674	-1.999246	-0.765641
17	C	-0.594193	-1.293756	0.248357
18	H	-0.331656	-2.194365	0.804047
19	H	-1.410890	-0.178437	2.086838
20	C	-1.212231	-0.085660	1.018364
21	C	-1.584915	-1.522356	-0.926991
22	H	-1.195311	-2.145882	-1.734313
23	C	-2.476813	0.256708	0.170103
24	H	-2.895040	1.245324	0.358515
25	C	-3.385866	-0.946363	0.417304
26	H	-4.242783	-0.948728	1.083985
27	C	-2.858510	-1.999664	-0.230694
28	H	-3.201990	-3.029182	-0.200571
29	C	-1.986694	-0.065898	-1.265620
30	H	-2.797839	-0.016689	-1.997538
31	H	-1.148812	0.548278	-1.608080

S4. Surface Reaction (3 water molecules)

Barrier = 13.7 kcal/mol at UB3LYP/6-31+G*

Barreir after ZPE correction = 14.7 kcal/mol

DMAD_w3

B3LYP/6-31+G* (E = -795.7045642973), <S2> = 0.00

1	C	3.853185	0.827087	-0.741823
2	O	2.456705	1.236817	-0.743290
3	C	1.763766	0.973526	0.347670
4	O	2.147276	0.503218	1.393652
5	N	0.395544	1.433176	0.151356
6	N	-0.408015	0.491416	0.111623
7	C	-1.795923	0.906541	-0.109963
8	O	-2.154332	1.521260	-1.079307
9	O	-2.522551	0.410460	0.879598
10	C	-3.959662	0.510177	0.718560
11	H	-4.247642	1.550698	0.554899
12	H	-4.257021	-0.114492	-0.125793
13	H	-4.374571	0.132015	1.652034
14	H	4.365506	1.277918	0.110971
15	H	4.251210	1.206033	-1.682010
16	H	3.902097	-0.262966	-0.697602
17	H	-1.708018	-2.326402	-0.842181
18	O	-2.518102	-1.908853	-1.198156
19	H	-2.476445	-2.027498	-2.158293
20	H	-0.337621	-2.800749	1.111043
21	O	-0.093702	-2.422454	0.251552
22	H	-0.154066	-1.446225	0.358819
23	H	1.887894	-2.520031	0.081805
24	O	2.834316	-2.298363	0.184023
25	H	2.870897	-1.781111	1.004230

TS_w3

B3LYP/6-31+G* (E = -1067.1356675938), <S2> = 0.00

1	C	-3.625041	-1.921919	-1.422554
2	O	-2.218112	-1.674117	-1.575071
3	C	-1.542051	-1.364899	-0.456039
4	O	-2.087480	-1.285207	0.649582
5	N	-0.184791	-1.238491	-0.762488
6	N	0.493070	-0.805113	0.262780
7	C	1.873509	-1.128304	0.263096
8	O	2.666347	-0.612939	1.039674
9	O	2.195343	-2.130247	-0.567565
10	C	3.547521	-2.615688	-0.470937
11	H	4.258173	-1.822931	-0.718704

12	H	3.748459	-2.979565	0.540183
13	H	3.607759	-3.429383	-1.194152
14	H	-3.799279	-2.702847	-0.677731
15	H	-3.966730	-2.244007	-2.406615
16	H	-4.146227	-1.008220	-1.120653
17	C	1.041626	2.963131	-0.415434
18	C	1.696826	1.712539	-0.813063
19	C	1.223951	1.363431	-2.229699
20	C	-0.214871	1.853998	-2.104674
21	C	-0.246544	3.033888	-1.165328
22	C	-0.698533	1.615343	-0.693659
23	C	0.546971	1.335188	0.134978
24	H	0.611017	1.391444	1.216123
25	H	-1.712042	1.407788	-0.372503
26	H	-0.906385	3.890212	-1.219637
27	H	-0.922601	1.795270	-2.924217
28	H	1.793272	1.914442	-2.987370
29	H	1.273027	0.291017	-2.438919
30	H	2.700119	1.492449	-0.459358
31	H	1.363446	3.623909	0.379721
32	H	0.517497	0.551104	3.313212
33	O	1.369305	1.018028	3.191934
34	H	1.923487	0.400363	2.680999
35	H	-1.553674	-0.803814	3.798458
36	O	-1.234900	-0.191659	3.118796
37	H	-1.283271	-0.682173	2.266943
38	H	-2.764642	1.201540	2.254675
39	O	-3.345426	1.207651	1.472878
40	H	-3.280162	0.286308	1.165562

Product_w3
B3LYP/6-31+G* (E = -1067.2624750445), <S2> = 0.00

1	C	0.115229	-4.154586	-1.077362
2	O	-0.525335	-2.870794	-0.947848
3	C	0.285386	-1.840685	-0.643799
4	O	1.499434	-1.934527	-0.509413
5	N	-0.445011	-0.674177	-0.580851
6	N	0.126188	0.449766	0.110871
7	C	0.882648	1.421589	-0.514202
8	O	1.044404	2.528299	-0.016426
9	O	1.447225	0.981681	-1.645485
10	C	2.424343	1.864728	-2.241984
11	H	1.969120	2.830460	-2.475087
12	H	3.265833	1.997777	-1.557748
13	H	2.738947	1.356097	-3.153524
14	H	0.864678	-4.125853	-1.872097

15	H	-0.688108	-4.846979	-1.329723
16	H	0.587826	-4.439542	-0.133997
17	C	-3.388692	1.547089	1.060613
18	C	-2.067837	1.860237	0.358244
19	C	-2.407175	1.378031	-1.075955
20	C	-2.946017	0.001553	-0.611839
21	C	-3.910229	0.448875	0.486776
22	C	-1.731602	-0.546814	0.184761
23	C	-1.132480	0.721280	0.866078
24	H	-0.966187	0.698516	1.941440
25	H	-1.933831	-1.418986	0.805234
26	H	-4.797250	-0.095998	0.794876
27	H	-3.337554	-0.677721	-1.371818
28	H	-3.182917	1.991111	-1.543152
29	H	-1.547079	1.308112	-1.749196
30	H	-1.668339	2.867362	0.477745
31	H	-3.764702	2.072858	1.932755
32	H	3.495647	0.971349	1.311831
33	O	3.820772	1.846548	1.022544
34	H	3.018769	2.391242	0.950842
35	H	3.595786	-1.408936	1.808764
36	O	2.834656	-0.828436	1.655757
37	H	2.427901	-1.137932	0.811373
38	H	1.260145	-1.091699	2.671196
39	O	0.345321	-1.272908	2.978393
40	H	0.419829	-1.477044	3.921975